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## PATENTS ACT 1990

## PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

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**[54] Invention Title:**

Gas Phase Fluorination by Means of Crystalline Catalysts

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## (12) PATENT ABSTRACT   (11) Document No: AU-A-80340/94
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(54) Title
GAS PHASE FLUORINATION BY MEANS OF CRYSTALLINE CATALYSTS

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(57) Claim

1.      Process for the gas phase catalytic fluorination of a saturated halogenated aliphatic hydrocarbon by means of hydrofluoric acid in the presence of a bulk or supported catalyst based on chromium oxide or oxides of chromium and at least one other catalytically active metal, in which the major part of the oxide(s) is in the crystalline state and, when the catalyst is a bulk catalyst, its specific surface, after activation with HF, is at least 8 $m^2/g$.

2.      Process according to Claim 1, in which the metal associated with the chromium is chosen from magnesium, nickel, zinc, iron, cobalt, vanadium and manganese.

5.      Process according to any one of Claims 1 to 4, in which the crystalline phase comprises the oxide $Cr_2O_3$, $CrO_2$, $NiCr_2O_4$, $NiCrO_3$, $NiCrO_4$, $MgCrO_4$, or $ZnCr_2O_4$ or a mixture of these oxides.

(11) 80340/94

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13.        A fluorinated hydrocarbon obtained by the
process claimed in any one of Claims 1 to 12.

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The present invention relates to the gas phase fluorination of halogenated hydrocarbons and its subject is more particularly a process for catalytic fluorination of saturated halogenated aliphatic

5    hydrocarbons by means of chromium-based crystalline catalysts.

Intensive investigations conducted into the substitutes for chlorofluorocarbons (CFCs) are directed, inter alia, towards the synthesis of

10   halogenated hydrocarbons which have more complex formulae and which are chemically more reactive. This new step forward in fluorination has resulted in the development of more active and, above all, more selective catalysts. Thus, chromium derivatives -

15   already renowned as good catalysts for gas phase fluorination - have been the subject of more specific preparations (precursors, operating conditions etc) to improve further their catalytic performance. In some cases the catalytic power of chromium has also been

20   strengthened by the addition of other metallic elements, such as cobalt, zinc, magnesium, iron, copper etc.

In the temperature range commonly employed for gas phase fluorination (200-450°C) the rate of

25   fluorination of the oxygen-containing chromium derivatives by hydrofluoric acid decreases

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exponentially as a function of the degree of fluorination of the catalyst. While an F/Cr atomic ratio of the order of 1.5 is rapidly reached, obtaining higher F/Cr atomic ratios (2.5 to 3 in the case of

5   Cr(III)) requires, on the other hand, either very long fluorination periods (> 100 hours), or operation at higher temperatures, with risks of degradation of the catalyst.

US Patent 3,426,009 describes the synthesis

10   of fluorinated compounds which is based on gas phase fluorination with HF with a chromium-based catalyst. This catalyst is obtained by thermal-reduction of $CrO_3$. The activity of the catalyst depends on the proportion of chromium in an oxidation state higher than 3, which

15   is present in the catalyst at the end of the heat treatment. It is clearly stipulated that this calcining in air must not exceed 370°C to avoid obtaining a $Cr_2O_3$ called "green chromium oxide", which is not active in fluorination (column 1, lines 65 to 70 and column 2,

20   lines 9 to 16).

The catalyst claimed in US Patent 3,992,325 is a trihydrated chromium(III) oxide. In this solid, considered for a long time to be amorphous, the authors have identified an orthorhombic crystalline phase

25   corresponding to a "gamma chromium oxide-hydroxide" structure, written "γ CrOOH". This crystalline phase has been found to be an excellent fluorination catalyst (column 1, lines 20 to 30). In most cases the catalyst

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must first of all be subjected to an activation (column 3, lines 55 to 65), and it is specified that the temperature during this activation must not exceed 500°C in order to avoid the formation of any other

5    crystalline phase of the chromium, which is inactive in fluorination (column 3, lines 65 to 68 and column 4, lines 1 and 2).

A specific preparation of a chromium catalyst, described in European Patent EP 514,932 A2

10    produces a chromium oxide of very large surface area (> 170 m$^2$/g). To exhibit a sufficient fluorination activity, this catalyst must be amorphous (page 3, lines 1 to 3 and lines 40 to 43) and must therefore have a large surface area. The authors explain that it

15    is necessary to avoid a calcination at excessively high temperature to limit the risk of crystallization of the chromium oxide (page 3, lines 35 to 40).

Only European Patent EP 548,742 A1 is known to describe the use of a crystalline chromium catalyst.

20    This type of catalyst is employed specifically for the purification of F134a by conversion of F1122 (CF$_2$=CHCl) into F133a (CF$_3$-CClH$_2$). The catalysts must have a crystallinity higher than 60 %. The chromium oxide Cr$_2$O$_3$ is either in bulk form or is supported on fluorinated

25    alumina. The advantage of this crystalline chromium oxide is based on the absence of emission of volatile and toxic chromium(VI) oxyfluorides during the regeneration (page 2, lines 42 to 44). In the case of

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this coke-generating purification (presence of F1122) the small surface area of the catalysts does not permit a lifetime without very long regeneration (regeneration every 24 hours).

5         The addition of "dopants" to improve the catalyst performance of chromium derivatives can, in some cases, also retard the crystallization of the catalyst. Thus, European Patent EP 546,883 A1 claims a mixed catalyst based on chromium and nickel oxides.

10    Although it is possible to introduce $Cr_2O_3$ (amorphous or crystalline) to improve the toughness of the catalyst, it is recommended to avoid excessively high temperatures capable of inducing a crystallization of the active part of the catalyst (page 4, lines 50 to

15    55).

        Similarly, US Patent 4,547,483 describes the preparation of a bulk catalyst by precipitation of a chromium(III) salt doped with a magnesium salt. In order to avoid a drop in reactivity of chromium oxide

20    towards HF and thus to facilitate the formation of fluorinated active species, the drying and the activation of the catalyst are always conducted at a temperature below 400°C (column 3, lines 64 to 69).

        Finally, European Patent EP 502 605 describes

25    a chromium catalyst promoted using a zinc-based compound. Here again, as with all the catalysts mentioned in the above examples, the catalytic activity is linked with completely or partially fluorinated

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species. In this particular case the active catalyst consists of zinc fluoride and chromium oxyfluorides and fluorides (page 3, lines 47 to 52). This is why it is desirable to pretreat these catalysts with HF before
5    employing them in fluorination.

Oxygen-containing chromium derivatives which have an amorphous structure react with fluorinating agents and, more particularly, with hydrofluoric acid. The rate of fluorination of these compounds decreases
10   exponentially as a function of the degree of fluorination of the catalyst. Thus, under the operating conditions generally employed in the gas phase (T < 450°C), the fluorination of chromium(III) can be divided into two stages:

15           - a rapid initial fluorination which makes it possible to reach an F/Cr atomic ratio of the order of 1.5 in a few hours,

            - a second stage which produces much more slowly (several hundred hours) an F/Cr atomic ratio
20   close to 3.

Since this fluorination of the catalyst with HF is exothermic, it requires a very gradual control (dilution in an inert substance, slow and controlled increase in temperature). Another disadvantage is that
25   it is accompanied by water formation which can, on the one hand, inhibit the catalytic activity and, on the other hand, give rise to high corrosion of the industrial tool in the presence of hydracids.

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This is why, in industrial practice, the rapid fluorination stage is generally carried out in the absence of any organic product capable of reacting with the fluorinating reactant (HF, etc); this

5    treatment is commonly called "catalyst activation". Because of the corrosion risks, this activation stage is frequently conducted in a simplified plant where the crude reaction product is treated directly in scrubbing columns, without recovery and recycling of the

10    unreacted fluorinating reactant.

This partially fluorinated solid already catalyses fluorination reactions; this is why, because of its excessively long duration, more extensive fluorination of the chromium catalyst often takes place

15    in the industrial unit for the fluorination of the organic product in the presence of the reaction mixture (organic substances, HF, HCl, etc). This perfluorination of the catalyst in the industrial reactor is not without its disadvantages:

20           - it makes it necessary either to stop the activation stage in operating conditions close to those of the unit for fluorination of the organic substances, or to carry out a very gradual start-up of the industrial unit, in order to spread out in time the

25    release of water and of heat due to the fluorination of the catalyst. This exothermicity is additional to the unavoidable exothermicity of the adsorption of HF on the catalyst;

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   - it presents risks of temperature runaway
with damage to the industrial tool and to the catalyst
charge; in fact, an excessively great thermal shock of
the fluorinated catalyst is often reflected in a

5    deterioration in its mechanical properties (formation
of powder);

   - finally, formation of large quantities of
water at point locations can result in rapid corrosion
of the crucial components of the industrial tool.

10       Hitherto, during the preparation and use of
catalysts based on chromium oxides or hydroxides, in
order to obtain acceptable catalytic performance it was
recommended to preserve the amorphous character by
avoiding heat treatments at excessively high

15   temperatures (> 450°C) and under oxidizing atmosphere.
       It has now been found that, provided that
they have a sufficiently large specific surface, highly
crystalline chromium oxides exhibit good activity for
the catalytic fluorination of saturated halogenated

20   aliphatic hydrocarbons.

       The presence of crystalline phases in the
"new" catalyst (virgin in respect of any fluorinating
treatment) limits its reactivity towards fluorine
compounds and especially HF. After a rapid activation

25   the catalysts are almost inert towards HF. Changing
very slightly during their use, they offer the
advantage of eliminating the risks of corrosion due to

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water formation. Furthermore, when compared with the amorphous catalysts, the crystalline catalysts are markedly less sensitive to thermal shocks, especially to temperature rises due to the production hazards.

5      According to the present invention, there is therefore provided a process for the gas phase catalytic fluorination of a saturated halogenated aliphatic hydrocarbon by means of HF in the presence of a bulk or supported catalyst based on chromium oxide or

10 oxides of chromium and of at least one other catalytically active metal, in which the major part of the oxide(s) is in the crystalline state and, when the catalyst is a bulk catalyst, its specific surface, after activation with HF, is at least 8 m$^2$/g.

15      As in the case of the amorphous catalysts of the prior art, the crystalline chromium catalysts used according to the invention can be doped by the presence of at least one other catalytically active metal (for example nickel, cobalt, manganese, magnesium, iron,

20 zinc, vanadium etc) to improve the catalytic performance and/or the physicochemical properties of the catalysts. The atomic ratio: other active metal/chromium is generally below 1.2 and is preferably between 0.1 and 1.

25      The catalysts according to the invention can be obtained from amorphous chromium catalysts by subjecting the latter, before or after they are formed, to a heat treatment in conditions which make it

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possible to obtain the crystallization of the active
species and to preserve a sufficient specific surface
(> 8 $m^2$/g after activation with HF)..

5    The crystallization atmosphere is an
important parameter. Although it may be possible to
work under an inert substance (nitrogen, argon, etc),
it is preferred to perform the heat treatment in an
oxidizing atmosphere (air, oxygen, etc) which makes it
possible to initiate the crystallization at lower
10   temperatures and to obtain a larger specific surface.
The treatment temperature is also important because it
directly affects the crystallization kinetics, the
crystallite size and the nature of the crystalline
phases. The minimum temperature for obtaining the
15   crystallization of the chromium oxide or of the oxides
of chromium and of the additional metal depends on the
metallic precursors employed and can be determined by
thermal or calorimetric analysis. In general, to
preserve a sufficient surface area, the temperature of
20   the treatment in air is between 300 and 750°C,
preferably between 400 and 700°C; in the case of an
undoped chromium oxide the temperature is
advantageously lower than 650°C.

The duration of the heat treatment is quite
25   obviously related to the abovementioned parameters, but
generally does not exceed 48 hours. In the majority of
cases heating for 0.5 to 24 hours makes it possible to
obtain the required crystalline solid. The temperature

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rise is preferably performed gradually (20 to
200°C/hour).

The starting amorphous catalysts can be
prepared by the different techniques known to a person
5    skilled in the art, which make it possible to obtain
solids of large specific surface, for example by
coprecipitation, in the form of hydroxides, of
different metal salts, or by reduction of $CrO_3$. Without
any limitation being implied, a preferred method for
10   the preparation of bulk amorphous catalysts includes
the following stages:

a) dissolving in water a chromium(III) salt
(for example chloride, sulphate or nitrate) and
optionally a precursor of at least one other metal, it
15   being possible for this precursor to be a salt (for
example chloride, nitrate, acetate, sulphate etc) or,
provided it is soluble in the mixture, a metal oxide or
hydroxide;

b) formation of a sol by partial
20   neutralization of the above solution with a base (NaOH,
$NH_4OH$, amines etc), it being possible for this
neutralization to be performed directly in the case of
the precursors of the acetate or sulphate type, or to
require heating between 60 and 95°C beforehand in the
25   case of the precursors of the nitrate or halide type;

c) gelling of the sol by neutralization or
basification to pH 6-11 (depending on the pH of
precipitation of the active co-metal(s)) by means of a

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base (NaOH, NH$_4$OH, amines, etc); and finally

d) washing the gel and drying between 50 and 200°C.

To complete the formation of the sol (stage
5   b), a complexing agent for the chromium and/or the
additional metals may be added to the aqueous solution
of the precursors, such as, for example, ammonium
acetate, sulphate or phosphate, in a quantity which can
be up to five times the total number of moles of the
10  precursors.

The gel in stage c can also be obtained by
reduction of CrO$_3$ in solution by means of a reducing
agent such as methanol.

The forming of the catalyst, effected before
15  or after the crystallization operation, can be carried
out in a manner known per se, for example by
tabletting, extrusion or granulation.

Various additives may also be added during
the preparation of the catalysts to enhance their
20  physicochemical and catalytic properties. It is thus
possible to add (% relative to the weight of the final
catalyst):

- 2 to 30 % of powdered Cr$_2$O$_3$ or Cr$_2$O$_3$·2H$_2$O
dried beforehand at 300°C, or Al$_2$O$_3$·xH$_2$O, to improve the
25  mechanical behaviour of the final catalyst,

- 0.1 to 5 % of graphite and/or 0.1 to 10 %
of polyvinyl alcohol, to facilitate the forming by
tabletting or extrusion,

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- 0.1 to 20 % of flocculant such as polyacrylates or polyacrylamides, to facilitate the filtration of the cake recovered after neutralization.

With a crystalline chromium catalyst

5  according to the invention the activation stage with HF can be considerably reduced. It is generally limited to a temperature rise under HF in the absence of organic substances. However, if the catalyst has not been crystallized directly in the fluorination reactor, it

10  is important to dry the catalyst under inert gas or in air before introducing HF, in order to eliminate any risk of corrosion. The temperature of this drying may be between 100°C and the temperature employed for the crystallization; it is preferred, however, to perform

15  the drying at a temperature of between 150°C and a temperature which is 50°C lower than that at which the crystallization has been performed.

Next, because of the heat of adsorption of HF on the catalyst, it is recommended to introduce this

20  reactant gradually, at a temperature of between 50°C and the temperature set for the fluorination reaction of the organic substances. It is generally preferred to perform the activation at a temperature of between 100 and 350°C and then, as soon as the HF adsorption peaks

25  have passed, it is possible to rise directly to the temperature required for the fluorination reaction of the organic compound being studied. As there is no risk of the catalyst being fluorinated, it is unnecessary to

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keep to plateaus at different temperatures. When the
catalyst is at the desired temperature it is possible
to commence the introduction of the organic reactants,
and these generally replace the inert gas employed for
5  the temperature rise.

When the catalyst contains additives which
react with the fluorinating agents it may be found
necessary to begin with activation to ensure the
fluorination of these compounds. However, given the low
10  proportions of this third substance and generally its
readiness to be fluorinated, the activation remains
limited in time. This case corresponds to that of
alumina, which is added to reinforce the mechanical
properties of the catalyst. It does not associate with
15  chromium but reacts with HF to form aluminium
oxyfluorides or trifluoride. This alumina is
fluorinated more readily than the chromium-based
compounds and a rapid activation of the catalyst with
HF at a temperature of 350-400°C makes it possible to
20  bind more than 80 % of the fluorine needed to convert
it into $AlF_3$. A catalyst is thus obtained which
effectively does not change further in the synthesis
reactor.

The crystalline catalysts according to the
25  present invention can be employed for the gas phase
fluorination of saturated halogenated aliphatic
hydrocarbons with HF. They are particularly suitable
for the fluorination of halogenated hydrocarbons

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resulting in $C_1$-$C_4$ fluorinated compounds containing one or more hydrogen atoms. As examples of starting halogenated hydrocarbons the following compounds may be mentioned, with no limitation being implied: $CHCl_3$,

5    $CH_2Cl_2$, $CH_2Cl$-$CFCl_2$, $CHCl_2$-$CFCl_2$, $CHCl_2$-$CClF_2$, $CH_2Cl$-$CF_2Cl$, $CH_3$-$CCl_3$, $CHCl_2$-$CF_3$, $CHFCl$-$CF_3$, $CH_2Cl$-$CF_3$, $CH_3$-$CCl_2$-$CH_3$, $CCl_3$-$CF_2$-$CH_3$, $CCl_3$-$CF_2$-$CHCl_2$, $CCl_3$-$CF_2$-$CH_2Cl$, $CHCl_2$-$CHCl$-$CH_3$ and $CH_2Cl$-$CHCl$-$CH_3$.

The temperature of the fluorination of the
10   organic substances depends on the reaction being studied and quite obviously on the desired reaction products. Thus, in the case of a partial substitution of chlorine atoms with fluorine, the work is done at temperatures of between 50 and 350°C, the substitution
15   of all the chlorine atoms generally requiring temperatures of between 300 and 500°C.

The contact time also depends on the reaction being studied and on the intended products. In most cases it is between 3 and 100 seconds; however, to
20   obtain a good compromise between the degree of conversion and space time yield, the contact time is advantageously shorter than 30 seconds.

The HF/organic compounds(s) molar ratio is also related to the reaction being studied. It depends,
25   among others, on the stoichiometry of the reaction. In most cases it can vary between 1/1 and 20/1 but, here again, it is frequently lower than 10 in order to obtain high space time yields.

15

The working pressure is preferably between 1 and 20 bars absolute (0.1 to 2 MPa).

Depending on their mechanical toughness, the catalysts according to the invention can work in a stationary bed or in a fluid bed. The catalysts whose activity has dropped as a consequence of fouling can be regenerated by purging the catalyst with a compound capable of oxidizing and converting the products (organic substances, coke etc) deposited on the catalyst as volatile products. Oxygen or a mixture containing oxygen (for example air) is perfectly suitable for this purpose and enables the initial activity of the catalyst to be restored. The exothermicity of this "combustion" must, of course, be controlled by controlling the flow rate of oxygen (at the beginning of regeneration a high dilution in an inert substance) to prevent a runaway of this regeneration and to avoid exceeding temperatures higher than 600°C. However, in contrast to the amorphous solids, the catalysts according to the invention are, as a result of their crystalline state, markedly less sensitive to temperature rises.

To maintain the activity of the catalyst it is also possible to perform the fluorination reaction in the presence of oxygen introduced in an $O_2$/organic compound molar ratio which may range from 0.001 to 0.05 and, preferably, is between 0.005 and 0.03. Here again, the crystalline catalysts are in a stable state to

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better withstand high temperatures in the presence of oxygen.

The following examples illustrate the invention without limiting it.

5       ## PREPARATION OF THE CATALYSTS

Catalyst 1 ($Cr_2O_3$ calcined in air at 400°C)

30 g (0.075 mol) of chromium nitrate nonahydrate $Cr(NO_3)_3 \cdot 9H_2O$ and 32 g (0.225 mol) of ammonium oxalate monohydrate were added to 75 ml of

10      water at ambient temperature and the mixture was then heated to 60°C until the ammonium oxalate was completely dissolved. The solution was then cooled to 20°C and then poured rapidly into a mixture of 375 ml of ethanol and 375 ml of ethylene glycol. The

15      precipitate obtained was filtered and then washed repeatedly with ethanol and dried at 80°C for 24 hours.

The solid obtained was then decomposed in air at 400°C for 5 minutes, the temperature rise being performed at a rate of 1°C/min.

20      Catalyst 2

Same preparation as catalyst 1, but with the calcination being performed at 600°C instead of 400°C.

A catalyst similar to catalyst 1 was obtained ($Cr_2O_3$ predominant crystalline phase), but with a BET

25      surface area of 16 m²/g.

Catalyst 3 (comparative)

160 g of $Cr_2O_3 \cdot 2H_2O$ were mixed with 276 g of

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an aqueous solution containing 12 % of polyvinyl alcohol, this alcohol facilitating the tabletting of this crystalline chromium oxide. After drying at 100°C for 15 hours the powder obtained was calcined in air at

5   400°C for 4 hours before being formed by tabletting.

Catalyst 4 (mixed Ni-Cr crystallized at 600°C)

80 ml of a 1M aqueous solution of chromium nitrate nonahydrate and 80 ml of a 1M aqueous solution

10   of nickel chloride hexahydrate were mixed at ambient temperature. The mixture was then heated to 80°C and then cooled before 3.8 g of $Al_2O_3 \cdot 2.4 H_2O$ were dispersed therein. The mixture was then neutralized by adding 50 ml of 14N aqueous ammonia. After filtration and

15   washing the product was dried at 100°C for 15 hours. 0.4 g of graphite and 5.1 g of an aqueous solution containing 12 % of polyvinyl alcohol were then added to the solid thus obtained. After renewed drying at 100°C for 15 hours the powder obtained was calcined in air

20   according to the following procedure:

- rise to 200°C (100°C/hour), then a one-hour plateau,

- rise to 350°C (100°C/hour), then a two-hour plateau,

25 - rise to 600°C (100°C/hour), then a four-hour plateau.

Catalyst 5 (mixed Ni-Cr crystallized at 500°C)

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Same preparation as catalyst 4 except for the final calcination temperature (500°C instead of 600°C).

Catalyst 6 (mixed Ni-Cr crystallized at 400°C)

5      Same preparation as catalyst 4 but with a final temperature of 400°C for the calcination.

Catalyst 7 (comparative: amorphous mixed Ni-Cr)

Same preparation as catalyst 4, but the
10      calcination in air up to 600°C is replaced by a heat treatment at 350°C under nitrogen.

Catalyst 8 (mixed Cr-V crystallized at 500°C)

20 g of Cr $(NO_3)_3 \cdot 9H_2O$ and 1.57 g of $VCl_3$ were introduced into 100 ml of water. The solution was then
15      neutralized to pH 6.4 with 14 ml of 14N aqueous ammonia. The gel thus formed was washed with water and then filtered off and dried in the oven at 120°C for 14 hours. The powder obtained was then calcined in air according to the following procedure:
20      -      rise to 200°C (100°C/hour), then one-hour plateau,

-      rise to 350°C (100°C/hour), then two-hour plateau,

-      rise to 500°C (100°C/hour), then four-hour
25      plateau.

Catalyst 9 (comparative: amorphous mixed Cr-V)

Same preparation as catalyst 8, but calcining

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the powder under nitrogen at 350°C for 4 hours.

Catalyst 10 (crystalline mixed Cr-Mg)

200 g (0.5 mol) of chromium nitrate nonahydrate and 26 g (0.1 mol) of magnesium nitrate

5 hexahydrate were dissolved in 1 litre of water. The mixture was heated to 80°C for 2 hours and then made basic to pH 10.2 by the addition of aqueous ammonia.

The gel obtained was washed twice with 450 ml of distilled water and then dried at 100°C for 14 hours

10 and finally calcined at 350°C in air for 4 hours.

Catalyst 11 (crystalline mixed Cr-Zn)

200 g of chromium nitrate nonahydrate and 68 g (0.5 mol) of zinc chloride were dissolved in 1 litre of water. The whole was heated to 80°C for 2

15 hours with stirring and then taken to pH 6.7 by the addition of aqueous ammonia.

The gel obtained was then washed twice with 450 ml of distilled water and then dried at 100°C for 14 hours and finally calcined in air at 400°C for 4

20 hours.

Catalyst 12 (comparative: amorphous mixed Cr-Zn)

Same preparation as catalyst 11, but with the final calcination performed at 300°C under nitrogen.

25 **ACTIVATION OF THE CATALYSTS AND FLUORINATION OF F133a**

The performance of catalysts 1 to 12 and that

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of a crystalline bulk $CrO_2$ (catalyst 13 hereinafter) was tested, after activation with HF, in the fluorination of 1-chloro-2,2,2-trifluoroethane (F133a) at atmospheric pressure.

5          The hydrofluoric acid employed is a commercial product containing only traces of water and the starting F133a is a 99.9% pure product. The reactor employed is a 20-ml Inconel tube heated by a tubular oven.

10          Before the fluorination test the catalyst (15 ml) placed in the reactor was first of all dried under nitrogen (5 l/h) for 2 hours at 250°C and then activated according to one or other of the following activation methods:

15          (a) Short activation at low temperature (for catalysts 1, 2, 3, 8 and 13)

HF is added gradually at 250°C to the nitrogen stream and then, after the exothermicity peaks due to the adsorption of HF on the catalyst have

20  passed, the latter is heated to the temperature chosen for the fluorination reaction.

Next, at this temperature and without keeping to any plateau, the nitrogen is gradually replaced with F133a and the flow rates are adjusted to obtain the

25  chosen HF/F133a molar ratio.

(b) Long activation at low temperature (for catalysts 7, 9, 10 and 12)

Same activation as above but a plateau of 10

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hours at 350°C is observed before introducing F133a.

(c) Activation at high temperature (for catalysts 4, 5, 6 and 11)

HF is added gradually at 250°C to the nitrogen stream and then, after the exothermicity peaks have passed, the catalyst is heated to 450°C (only 400°C in the case of catalyst 6 and 350°C in the case of catalyst 10). After a plateau of 6 hours at this temperature the latter is returned to 350°C and the nitrogen is gradually replaced with F133a to adjust the flow rates to the chosen HF/F133a molar ratio.

Before being introduced into the reactor the reactants are mixed and heated to the reaction temperature in an Inconel preheater.

After washing with water (removal of the hydracids) and drying over $CaCl_2$ the reaction products are analysed in line by gas phase chromatography.

The characteristics of each catalyst before activation (new catalyst) and after activation with HF are assembled in Table 1 which follows. The pore volumes shown were determined by mercury porosimetry and correspond to the volume of the pores of radius of between 4 nm and 63 μm.

The operating conditions and the results obtained in the tests for fluorination of F133a to F134a are collated in Table II.

Table III gives the characteristics of the spent catalysts 4, 7 and 13, that is to say after the

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fluorination tests F9, F14 and F5 respectively.

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## TABLE I

| CATALYST No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **New catalyst** | | | | | | | | | | Cr/Mg 5/1 | Cr/Zn 1/1 | Cr/Zn 1/4 | |
| - BET surface area (m²/g) | 28 | 16 | 41 | 56 | 72 | 36 | 107 | 47.4 | 213.7 | 140 | 62 | 145 | 28 |
| - pore volume (ml/g) | NM | NM | NM | 0.49 | 0.43 | 0.27 | 0.16 | 0.68 | 0.48 | 0.82 | 0.77 | 0.95 | NM |
| - predominant crystalline phase(s) | $Cr_2O_3$ | $Cr_2O_3$ | $Cr_2O_3$ | $NiCr_2O_4$ | $NiCrO_3$ and $Cr_2O_3$ | $NiCrO_4$ and $Cr_2O_3$ | (*) | $Cr_2O_3$ $Cr/V$ | (*) | $MgCrO_4$ and $Cr_2O_3$ | $ZnCr_2O_4$ | (*) | $CrO_2$ |
| Calcination T. in air | 400°C oxalate | 600°C oxalate | 400°C PVA | 600°C 1:1 | 600°C | 400°C | 350°C/H₂ | 500°C | 350°C/N₂ | 350°C | 400°C | 350°C/N₂ | |
| **Activated catalyst** | | | | | | | | | | | | | |
| - activation method | a | a | a | c | c | c | b | a | b | b | c | b | a |
| - BET surface area (m²/g) | 27.7 | 15 | 6.7 | 36.4 | 61.6 | 55 | 36.3 | 32.3 | 43.4 | 50.1 | 45.2 | 79.4 | 39.7 |
| - weight analysis CrX | 60.6 | 65.8 | 59.7 | 27.6 | 27.4 | 27.C | 21.2 | 54.5 | 45.9 | 50.8 | 28.7 | 30.1 | 60.3 |
| Cometal:X | - | - | - | Ni:30.3 | Ni:29.5 | Ni:29.8 | Ni:22.9 | V:7.9 | V:7.1 | Mg:5.9 | Zn:34.7 | Zn:36.8 | - |
| Al% | - | - | - | 7 | 6.9 | 7.2 | 7.5 | - | - | - | - | - | - |
| F% | 1.9 | 0.7 | 3.1 | 15 | 16 | 14.5 | 29.3 | 3.5 | 19.7 | 19.9 | 3.1 | 15.1 | 2.5 |

NM = not measured
(*) amorphous catalyst

Activation:
a  Short activation at low temp, 250°C, 355°C then 133a
b  long activation at low temp. 350°C/16h
c  high temp activation 450°C (4o°c #6, 350e #10)

## TABLE II

Fluorination of F133a to F134a at 350°C and atmospheric pressure

| TEST | F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 | F10 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Operating conditions:** | | | | | | | | | | |
| Catalyst No. | 1 | 2 | 13 | 13 | 13 | 3 | 4 | 4 | 4 | 5 |
| HF/F133a molar ratio | 3.2 | 3.6 | 4 | 4 | 4 | 3.9 | 4.1 | 3.9 | 4.1 | 4.1 |
| $O_2$/F133a molar ratio | 0 | 0 | 0 | 0.005 | 0.01 | 0 | 0 | 0.01 | 0.01 | 0 |
| Contact time (seconds) | 2.5 | 4.3 | 4.2 | 0.5 | 0.5 | 4.1 | 4.1 | 0.8 | 0.8 | 4 |
| Catalyst age (hours) | 24 | 23 | 24 | 24 | 186 | 18 | 48 | 168 | 405 | 24 |
| **Results:** | | | | | | | | | | |
| Overall degree of conversion of F133a (%): | 20 | 13.5 | 20.7 | 14.8 | 13.2 | 0.3 | 19.5 | 16.3 | 13 | 20 |
| **Selectivity (mol%) for:** | | | | | | | | | | |
| - F134a ($CF_3CH_2F$) | 94.5 | 97.6 | 94.9 | 89.9 | 90.6 | 22 | 98.1 | 95.5 | 96.1 | 97.6 |
| - F1122 ($CF_2=CHCl$) | 1.5 | 1.3 | 0.4 | 2.8 | 3 | 50 | 1 | 2.9 | 3.1 | 1 |
| - F120 series (*) | 1.1 | 0.5 | 1.9 | 6.9 | 5.2 | 22 | 0.3 | 0.6 | 0.6 | 0.3 |
| - F143a ($CF_3CH_3$) | 2.5 | 0.4 | 2.5 | 0.2 | 0.3 | 3 | - | - | - | - |
| - Others | 0.5 | 0.2 | 0.3 | 0.2 | 0.7 | 3 | 0.7 | 1.1 | 0.4 | 1 |

* Combined hydropentahaloethanes

## TABLE II (Contd.)

Fluorination of F133a to F134a at 350°C and atmospheric pressure

| TEST | F11 | F12 | F13 | F14 | F15 | F16 | F17 | F18 | F19 |
|---|---|---|---|---|---|---|---|---|---|
| **Operating conditions:** | | | | | | | | | |
| Catalyst No. | 6 | 7 | 7 | 7 | 8 | 9 | 10 | 11 | 12 |
| HF/F133a molar ratio | 4 | 4 | 4 | 3.9 | 4.1 | 4 | 4 | 3.5 | 4.1 |
| O$_2$/F133a molar ratio | 0 | 0 | 0.01 | 0.01 | 0.005 | 0.005 | 0 | 0 | 0 |
| Contact time (seconds) | 4 | 4.3 | 0.5 | 0.5 | 0.5 | 0.5 | 4 | 4 | 4 |
| Catalyst age (hours) | 25 | 48 | 48 | 288 | 162 | 133 | 24 | 21 | 22 |
| **Results:** | | | | | | | | | |
| Overall degree of conversion of F133a (%): | 20.9 | 20.5 | 15.4 | 12.4 | 18.7 | 20.1 | 21.9 | 15.1 | 16.3 |
| Selectivity (mol%) for: | | | | | | | | | |
| - F134a (CF$_3$CH$_2$F) | 96.1 | 96.7 | 95.3 | 95.9 | 93 | 93.3 | 95.7 | 97.9 | 98.1 |
| - F1122 (CF$_2$=CHCl) | 1.2 | 1.3 | 2.5 | 2.2 | 1.8 | 1.6 | 0.9 | 1.4 | 1.3 |
| - F120 series (*) | 1.7 | 1 | 1.5 | 0.7 | 4.2 | 3.3 | 1.7 | 0.5 | 0.4 |
| - F143a (CF$_3$CH$_3$) | - | - | - | - | 0.3 | 0.2 | 1 | 0.1 | 0 |
| - Others | 0.9 | 0.9 | 0.7 | 0.2 | 0.7 | 1.4 | 0.7 | 0.1 | 0.2 |

* Combined hydropentahaloethanes

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## TABLE III

### Characteristics of the spent catalysts

| CATALYST NO. | 4 | 7 | 13 |
|---|---|---|---|
| Age (hours) | 405 | 288 | 186 |
| BET surface area ($m^2/g$) | 32.4 | 25.6 | 49.4 |
| Weight analysis: | | | |
| Cr% | 25.7 | 19.2 | 60.7 |
| Ni% | 27.3 | 21 | – |
| Al% | 7 | 6.3 | – |
| F % | 18.3 | 33.5 | 3.5 |

Tests F1, F2 and F3 show that it is possible to obtain good catalytic results, close to the thermodynamic equilibrium, with crystalline bulk catalysts of low fluorine content but which after activation have a surface area greater than 8 $m^2/g$.

In catalysts 1 and 2 the chromium is very predominantly in the oxidation state of III. On the other hand, in catalyst 13 in Tests F3, F4 and F5 the chromium is in the oxidation state of IV. Very good catalytic results are nevertheless obtained; a lifetime of 186 hours (Tests F4 and F5) even shows a very good stability of this activity.

Test F6 shows that a crystalline chromium oxide exhibiting a specific surface that is too low

after activation (catalyst 3) results in a very low
activity.

Tests F7 to F11 show the influence of the
crystallization temperature of a bulk Ni-Cr catalyst on
5      its catalytic activity. The results obtained with a
contact time of 4 seconds (Tests F7, F10 and F11) show
that the optimum crystallization temperature (best
compromise between fluorination of the catalyst during
the activation and catalytic activity) is between 500·
10     and 600 °C. It is also found that catalyst 4, calcined
at 600°C, exhibits a relatively stable activity (Tests
F8 and F9); the slight deactivation observed is due
solely to an initiation of coking of the catalyst
because of a slightly low $O_2$/F133a ratio. On the other
15     hand, if the fluorine contents of catalyst 4 are
compared at different stages (Tables 1 and III), it is
found that this content effectively does not change
further after activation; the change from 15 to 18 %
over 400 hours of test corresponds to the fluorination
20     of the alumina present in the catalyst, the active
constituents of the catalyst (chromium and nickel
derivatives) not being fluorinated, or very slightly
so.

When tested in similar operating conditions,
25     the amorphous Ni-Cr catalyst (catalyst 7) has an
activity equivalent to that of the crystalline Ni-Cr
catalyst. However, it is deactivated more rapidly and,
above all, its fluorination continues during the

fluorination test to reach 33.5 % of fluorine after only 288 hours of test.

Tests F15 and F16 make it possible to compare the catalytic activities of bulk catalysts based on

5    chromium and vanadium, one being in amorphous form (catalyst 9), the other being crystalline (catalyst 8). Although slightly less active than its amorphous homologue, the crystalline catalyst has the advantage of being fluorinated very slightly; 3.5 % of fluorine

10   after activation (19.7 % in the case of the amorphous catalyst).

The claims defining the invention are as follows:

1.      Process for the gas phase catalytic fluorination of a saturated halogenated aliphatic hydrocarbon by means of hydrofluoric acid in the

5    presence of a bulk or supported catalyst based on chromium oxide or oxides of chromium and at least one other catalytically active metal, in which the major part of the oxide(s) is in the crystalline state and, when the catalyst is a bulk catalyst, its specific

10   surface, after activation with HF, is at least 8 m²/g.

2.      Process according to Claim 1, in which the metal associated with the chromium is chosen from magnesium, nickel, zinc, iron, cobalt, vanadium and manganese.

15   3.      Process according to Claim 2, in which the atomic ratio of other active metal/chromium is below 1.2.

4.      Process according to Claim 2, in which the atomic ratio of other active metal/chromium is between

20   0.1 and 1.

5.      Process according to any one of Claims 1 to 4, in which the crystalline phase comprises the oxide $Cr_2O_3$, $CrO_2$, $NiCr_2O_4$, $NiCrO_3$, $NiCrO_4$, $MgCrO_4$, or $ZnCr_2O_4$ or a mixture of these oxides.

25   6.      Process according to any one of Claims 1 to 5, in which the catalyst is obtained by subjecting an amorphous catalyst to heat treatment under conditions

sufficient to obtain the crystallization of the active species.

7.       Process according to Claim 6, in which the treatment is performed under inert or oxidizing atmosphere at a temperature of between 300 and 750°C.

8.       Process according to Claim 6, in which the treatment is performed under inert or oxidizing atmosphere at a temperature of between 400 and 700°C.

9.       Process according to any one of Claims 1 to 8, in which, before the fluorination of the saturated halogenated aliphatic hydrocarbon, the catalyst is activated by means of HF at a temperature of between 100 and 350°C.

10.       Process according to anyone of Claims 1 to 9, in which the halogenated hydrocarbon to be fluorinated is a $C_1$-$C_4$ compound containing one or more hydrogen atoms.

11.       Process according to any one of Claims 1 to 9 in which 1-chloro-2,2,2-trifluoroethane is fluorinated to 1,1,1,2-tetrafluoroethane.

12.       Process according to Claim 1, substantially as described in the Examples.

13.       A fluorinated hydrocarbon obtained by the process claimed in any one of Claims 1 to 12.

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# ABSTRACT

## GAS PHASE FLUORINATION BY MEANS OF
## CRYSTALLINE CATALYSTS

The invention relates to the gas phase catalytic fluorination of saturated halogenated aliphatic hydrocarbons by means of HF.

A bulk or supported catalyst is employed, based on chromium oxide or oxides of chromium and of at least one other catalytically active metal, in which the major part of the oxide(s) is in the crystalline state. In the case of a bulk catalyst, the specific surface, after activation with HF, is at least 8 $m^2/g$.

Using this catalyst, good catalytic performance is achieved.